

Lubricant Grease for Low and High Temperature

Application and Rolling Bearing

Background of the invention

5 The present invention relates to lubricant grease for low and high temperature application and to a rolling bearing. More particularly, the present invention relates to the lubricant grease that can be applied suitably for electric auxiliaries used for cars at low and high temperatures and the rolling bearing.

10 The lubricant grease is sealed in the rolling bearing to impart lubricant property thereto. The lubricant grease is obtained by kneading a base oil and a thickening agent both serving as its main component. As the base oil, mineral oil and synthetic oil such as ester oil, silicone oil, and ether oil are used. As 15 the thickening agent, metal soap such as lithium soap and urea compounds are generally used. The lubricant grease contains additives such as an antioxidant, a rust preventive, a metal deactivator, and a viscosity index improver as necessary.

20 In recent years, there are growing demands for production of a car which is compact, lightweight, and has low degree of noise. Therefore efforts are made to produce electric component parts for the car which are compact, lightweight, and have low degree of noise and make the interior of the engine room airtight. To do so, the electric component parts are required to have high 25 output and efficiency. Because the life of the lubricant grease

to be sealed in the rolling bearing is shorter than the life of the rolling bearing caused by its fatigue, the life of the rolling bearing depends on the life of the lubricant grease. Therefore the temperature to which the lubricant grease used for electric auxiliaries is resistant should be higher than the temperature to which urea-containing lubricant grease is resistant.

Heretofore heat-resistant fluorine-containing lubricant grease containing fluorocarbon resin powder as its thickening agent and perfluoropolyether oil as its base oil is used as grease to be sealed in the rolling bearing for use in a fan clutch which is heated to high temperatures in the neighborhood of 200°C. But the fluorine-containing lubricant grease is expensive and prevents reduction of the cost of the rolling bearing.

Therefore hybrid grease containing a mixture of the fluorine-containing lubricant grease and the urea-containing lubricant grease has been developed, as disclosed in Japanese Patent Laid-Open Nos. 2002-327759, 2004-3596, and 2004-26941. A lubricant grease composition having a preferable noise-reducing effect at temperatures of 180°C to 250°C is also known, as disclosed in Japanese Patent Laid-Open No. 2000-514105.

However, the conventional fluorine-containing lubricant grease generates noises at low temperatures when the fluorine-containing lubricant grease is used for electric auxiliaries.

When the viscosity of the base oil is reduced to restrain

noises from being generated at low temperatures by the fluorine-containing lubricant grease, noises are decreased at low temperatures. But the fluorine-containing lubricant grease containing the base oil is not durable at high temperatures in
5 the neighborhood of 200 °C.

Summary of the Invention

The present invention has been made to cope with the above-described problems. Accordingly, it is an object of the
10 present invention to provide lubricant grease, for low and high temperature application, which is durable owing to high resistance to high temperatures and capable of restraining noises from being generated at low temperatures and a rolling bearing in which the lubricant grease is sealed.

15 The lubricant grease, according to the present invention, for low and high temperature application includes 100 parts by weight of mixed grease and 3 to 30 parts by weight of polyolefin oil added to the mixed grease. The mixed grease contains fluorine-containing lubricant grease containing (a) perfluoropolyether oil as a base oil thereof and fluorocarbon resin powder as a thickening agent thereof and (b) urea-containing lubricant grease containing polyester oil as a base oil thereof and a urea compound as a thickening agent thereof.

20 The polyolefin oil has a pour point of not more than -50°C and a kinematic viscosity of 10 to 70 mm²/s at 40°C.
25

The urea-containing lubricant grease has a evaporation amount not more than 25 wt%, when the urea-containing lubricant grease is left at 200 °C for 250 hours.

The polyester oil is an aromatic ester compound of 5 monovalent alcohol having 7 to 22 carbon atoms and aromatic tricarboxylic or tetracarboxylic acid or derivatives thereof and/or an aliphatic ester compound of monovalent carboxylic acid having 7 to 22 carbon atoms and trimethylolpropane, pentaerythritol or dipentapentaerythritol.

10 The polyester oil is an aromatic ester compound of monovalent alcohol having 7 to 22 carbon atoms and aromatic tricarboxylic or tetracarboxylic acid or derivatives thereof.

The rolling bearing of the present invention has an inner ring, an outer ring concentric with the inner ring, a plurality 15 of rolling elements disposed between the inner ring and the outer ring, and lubricant grease sealed on the periphery of the rolling elements. The lubricant grease to be sealed is the above-described grease for low and high temperature application.

By adding 3 to 30 parts by weight of the polyolefin oil 20 to 100 parts by weight of the mixture of the fluorine-containing lubricant grease containing the perfluoropolyether oil as its base oil and the fluorocarbon resin powder as its thickening agent and the urea-containing lubricant grease containing the polyester oil as its base oil and the urea compound as its thickening agent, 25 it is possible to keep the fluorine-containing lubricant grease

heat-resistant and suppress the generation of noises at low temperatures. By using the aromatic ester compound as the polyester oil, it is possible to reduce the cost of manufacturing the lubricant grease.

5

Brief Description of the Drawings

Fig. 1 is a sectional view showing a deep groove ball bearing.

Detailed Description of the Preferred Embodiments

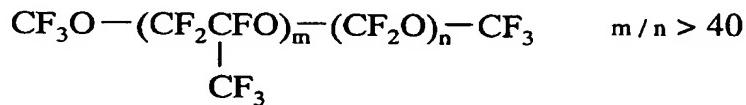
10 Fluorine-containing lubricant grease that can be used in the present invention contains perfluoropolyether oil as its base oil and fluorocarbon resin powder as its thickening agent.

As the perfluoropolyether oil, it is possible to use compounds formed by replacing hydrogen atoms of aliphatic hydrocarbon polyether with fluorine atoms. As perfluoropolyether oil having this structure, perfluoropolyether, shown by chemical formulas 1 and 2, having side chains and straight-chain perfluoropolyether shown by chemical formulas 3 through 5 can be used. These perfluoropolyethers can be used singly or as a mixture. Reference symbols n and m of the chemical formulas 1 through 5 indicate integers.

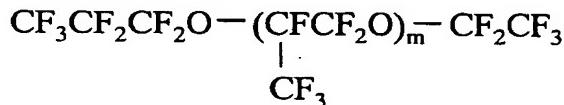
20 As the perfluoropolyether oil shown by the chemical formula 1, Fomblin Y (commercial name: produced by Solvay Solexis Inc.) is commercially available. As the perfluoropolyether oil shown

by the chemical formula 2, Krytox (commercial name: produced by Du-Pont Inc.) and Barrierta J oil (commercial name: produced by KLUEBER Inc.) are commercially available. As the perfluoropolyether oil shown by the chemical formula 3, Fomblin 5 Z (commercial name: produced by Solvay Solexis Inc.) is commercially available. As the perfluoropolyether oil shown by the chemical formula 4, Fomblin M (commercial name: produced by Solvay Solexis Inc.) is commercially available. As the perfluoropolyether oil shown by the chemical formula 5, Demnum 10 (commercial name: produced by Daikin Industries , Ltd.) is commercially available.

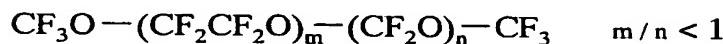
Chemical formula 1



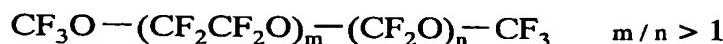
Chemical formula 2



15 Chemical formula 3



Chemical formula 4



Chemical formula 5



As for the fluorocarbon resin powder, it can be served as the

thickening agent of the fluorine-containing lubricant grease, under the condition of high affinity for the perfluoropolyether oil , good stability at high temperatures and resistance to chemicals.

5 As fluorocarbon resin, the following perfluorocarbon resins are preferable: polytetrafluoroethylene (PTFE), tetrafluoroethylene-perfluoroalkylvinyl ether copolymer (PFA), and tetrafluoroethylene-hexafluoropropylene copolymer (FEP). The polytetrafluoroethylene (PTFE) is particularly preferable
10 because it is excellent in stability at high temperatures and resistance to chemicals.

It is preferable that for 100 wt% of the entire amount of the fluorine-containing lubricant grease, 70 to 90 wt% of the perfluoropolyether oil and 10 to 30 wt% of the fluorocarbon resin
15 powder are mixed with each other. This mixing ratio allows the fluorine-containing lubricant grease to have a penetration at which it has a small leak amount and a low torque which can be kept for a long time, when the fluorine-containing lubricant grease is sealed in a rolling bearing.

20 Urea-containing lubricant grease that can be used in the present invention contains polyester oil as its base oil and an urea compound as its thickening agent.

As the polyester oil serving as the base oil of the urea-containing lubricant grease, at least one of the following
25 esters is used: ester of aliphatic monovalent alcohol having 7

to 22 carbon atoms and aromatic tricarboxylic or tetracarboxylic acid or derivatives thereof and ester of aliphatic monovalent carboxylic acid having 7 to 22 carbon atoms and trimethylolpropane, pentaerythritol or dipentapentaerythritol. In addition, 5 polymer ester may be used as the base oil of the urea-containing lubricant grease.

The aliphatic monovalent alcohol and the aliphatic monovalent carboxylic acid having less than 7 or more than 22 carbon atoms are inferior in lubricating properties.

10 As the aliphatic monovalent alcohol having 7 to 22 carbon atoms, it is possible to use heptyl alcohol, octyl alcohol, nonyl alcohol, decyl alcohol, undecylic alcohol, lauryl alcohol, oleyl alcohol, and stearyl alcohol and the like.

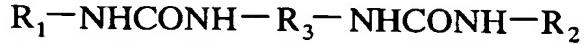
As the aliphatic monovalent carboxylic acid having 7 to 15 22 carbon atoms, it is possible to use monovalent carboxylic acid obtained by replacing a group $-CH_2OH$ of the aliphatic monovalent alcohol with a group $-COOH$.

As the aromatic tricarboxylic acid, the aromatic tetracarboxylic acid, and derivatives thereof, it is possible 20 to use trimellitic acid, trimesic acid, pyromellitic acid, biphenyltetracarboxylic acid, benzophenonetetracarboxylic acid, and acid anhydride thereof.

The urea-containing lubricant grease that can be used in the present invention contains the urea compound as its thickening 25 agent.

As the urea compound, diurea having two urea bonds in its molecule is preferable and is shown by a chemical formula 6 shown below:

Chemical formula 6



5 where R_3 is an aromatic group; R_1 and R_2 are selected one among an aliphatic group, an alicyclic group, and an aromatic group respectively ; R_1 and R_2 are to be the same or different from each other. As a method of producing the urea compound, a diisocyanate compound and an amine compound having an equivalent weight of
10 isocyanate group are reacted with each other.

In addition to the diurea, polyurea or the like can be also used as the thickening agent of the urea-containing lubricant grease.

It is preferable that for 100 wt% of the entire amount of
15 the urea-containing lubricant grease, 70 to 95 wt% of the ester oil and 30 to 5 wt% of the urea compound are mixed with each other. This mixing ratio allows the urea-containing lubricant grease to have a penetration at which it has a small leak amount and preferable lubricating properties which can be kept for a long
20 time, when the urea-containing lubricant grease is sealed in a bearing.

The evaporation amount of the urea-containing lubricant grease is not more than 25 wt%. If the evaporation amount is more than 25 wt%, it is impossible to make the evaporation amount

of a mixture of the urea-containing lubricant grease and the fluorine-containing lubricant grease low, for example, not more than 15 wt%.

In the present invention, in finding the evaporation amount,
5 after about 5g of grease is collected in a beaker made of glass
having a volume of 50ml conforming to the Japanese Industrial
Standard (JIS) R3503, the grease is left for 250 hours in a
constant-temperature oven (internal volume: 90 liters, air flow:
5.1m³/min, wind velocity: 0.42m/s), with internal air circulation,
10 set to 200 °C. The initial weight of the grease and the weight
thereof after it is left for 250 hours are measured to find the
evaporation amount from an equation shown below:

$$\text{Evaporation amount (\%)} = \{(\text{Initial weight} - \text{Weight after left for 250 hours}) / \text{Initial weight} \} \times 100$$

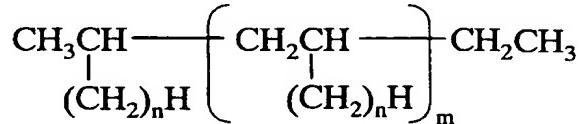
15 A mixture of the urea-containing lubricant grease and the fluorine-containing lubricant grease contains in the range from 30 wt% to 75 wt% of the urea-containing lubricant grease. If the mixing ratio of the urea-containing lubricant grease exceeds 75 wt%, the evaporation amount of the mixed grease increases.
20 If the mixing ratio of the urea-containing lubricant grease is less than 30, it is impossible to reduce the cost of manufacturing the lubricant grease.

In the present invention, polyolefin oil having a pour point of not more than -50 °C and a kinematic viscosity of 10 to 70
25 mm²/s at 40 °C is added at 3 to 30 parts by weight, favorably

3 to 20 parts by weight, more favorably 3 to 15 parts by weight to 100 parts by weight of the mixture of the fluorine-containing lubricant grease and the urea-containing lubricant grease. When the mixing ratio of the polyolefin oil is less than 3 parts by 5 weight, the lubricant grease is heat-resistant, but causes noises to be generated at low temperatures. When the mixing ratio of the polyolefin oil is more than 30 parts by weight, the lubricant grease does not cause noises to be generated at low temperatures but is inferior in heat resistance.

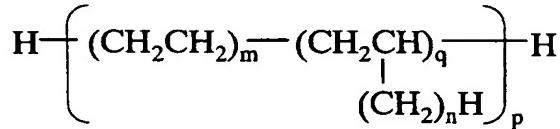
10 The polyolefin oil that can be used in the present invention is liquid polyolefin shown by chemical formulas 7 and 8:

Chemical formula 7



where n is integers of 4 to 16, and m is integers of 1 to 6.

Chemical formula 8



15 where n is integers of 1 to 8, m is integers of 1 to 3, q is integers of 1 to 3, and p is integers which vary in dependence on the viscosity of the polyolefin oil.

The polyolefin oil stays liquid at ordinary temperature.

20 The polyolefin oil has a pour point of not more than -50 °C and a kinematic viscosity of 10 to 70 mm²/s at 40°C. Because the polyolefin oil has a kinematic viscosity of 10 to 70 mm²/s, it

is capable of restraining noises from being generated at low temperatures and is heat-resistant.

Fig. 1 shows an example of the rolling bearing of the present invention. Fig. 1 is a sectional view of a deep groove ball bearing.

5 A rolling bearing 1 includes an inner ring 2 having an inner ring rolling surface 2a on its peripheral surface, an outer ring 3 concentric with the inner ring 2 and having an outer ring rolling surface 3a on its inner peripheral surface, and a plurality of rolling elements 4 disposed between the inner ring rolling surface 10 2a and the outer ring rolling surface 3a. The rolling bearing 1 further includes a holder 5 holding the rolling elements 4 and a sealing member 6 fixed to the outer ring 3. A grease 7 for low and high temperature application is sealed on ,at least , the periphery of the rolling elements 4.

15 The lubricant grease 7 is durable owing to high resistance to high temperatures and capable of restraining noises from being generated at low temperatures. Therefore the lubricant grease 7 can be applied suitably for rolling bearings of electric component parts of a car such as an alternator, an electromagnetic 20 clutch for a car air conditioner, an intermediate pulley, an electromotive fan motor, a fan clutch and electric auxiliaries.

Example

Reference Example 1: Preparation of grease 1

25 For 100 wt% of the entire amount of the grease, 33 wt% of

fluorocarbon resin powder was added to 67 wt% of perfluoropolyether oil having a kinematic viscosity of 191 mm²/s at 40 °C. Thereafter the mixture was stirred and supplied to a roll mill. Thereby a semisolid grease 1 containing the 5 fluorocarbon resin powder serving as its thickening agent and perfluoropolyether oil serving as its base oil was obtained.

Reference Example 2: Preparation of grease 2

For 100 wt% of the entire amount of the grease, 33 wt% of fluorocarbon resin powder was added to 67 wt% of 10 perfluoropolyether oil having a kinematic viscosity of 90 mm²/s at 40 °C. Thereafter the mixture was stirred and supplied to the roll mill. Thereby a semisolid grease 2 containing the fluorocarbon resin powder serving as its thickening agent and perfluoropolyether oil serving as its base oil was obtained.

15 Reference Example 3: Preparation of grease 3

For 100 wt% of the entire amount of the grease, one mol of diphenylmethane diisocyanate was dissolved in one half amount of 88 wt% of aromatic ester oil having a kinematic viscosity of 91 mm²/s at 40 °C. Thereafter two mols of octylamine was dissolved 20 in the other half amount of the aromatic ester oil. The mixture of the octylamine and the aromatic ester oil was added to the base oil containing the diphenylmethane diisocyanate and the aromatic ester oil, while stirring was being carried out. The stirring continued for reaction at 100 to 120 °C for 30 minutes.

25 As a result, 12 wt% of an urea compound deposited in the base

oil. Thereafter the mixture was supplied to the roll mill. Thereby a semisolid grease 3 containing the urea compound serving as its thickening agent and the aromatic ester oil serving as its base oil was obtained. When the grease 3 was left at 200
5 °C for 250 hours, the evaporation amount of the grease 3 was 17.4 wt%.

Reference Example 4: Preparation of grease 4

For 100 wt% of the entire amount of the grease, one mol of diphenylmethane diisocyanate was dissolved in one half amount
10 of 80 wt% of alkyl diphenyl ether having a kinematic viscosity of 100 mm²/s at 40 °C. Thereafter two mols of p-toluidine was dissolved in the other half amount of the alkyl diphenyl ether. The mixture of the p-toluidine and the alkyl diphenyl ether was added to the base oil containing the diphenylmethane diisocyanate
15 and the alkyl diphenyl ether, while stirring was being carried out. The stirring continued for reaction at 100 to 120°C for 30 minutes. As a result, 20 wt% of an urea compound deposited in the base oil. Thereafter the mixture was supplied to the roll mill. Thereby a semisolid grease 4 containing the urea compound
20 serving as its thickening agent and the alkyl diphenyl ether serving as its base oil was obtained. When the grease 4 was left at 200 °C for 250 hours, the evaporation amount of the grease 4 was 31.0 wt%.

Polyolefin oil used in each of the examples and comparison
25 examples is shown below.

- Polyolefin oil 1: The pour point is -57 °C. The kinematic viscosity at 40 °C is 46 mm²/s. The kinematic viscosity at 100 °C is 7.8 mm²/s (produced by Nippon Steel Chemical Co.,Ltd., commercial name; Shinfluid 801).
- 5 • Polyolefin oil 2: The pour point is -73 °C. The kinematic viscosity at 40 °C is 17 mm²/s. The kinematic viscosity at 100 °C is 3.9mm²/s (produced by Nippon Steel Chemical Co.,Ltd., commercial name; Shinfluid 401).
- 10 • Polyolefin oil 3: The pour point is -53 °C. The kinematic viscosity at 40 °C is 63 mm²/s (produced by Idemitsu Petrochemical Co., Ltd., commercial name; Idemitsu PAO 5010).
- 15 • Polyolefin oil 4: The pour point is -73 °C. The kinematic viscosity at 40 °C is 5 mm²/s. The kinematic viscosity at 100 °C is 1.7 mm²/s (produced by Nippon Steel Chemical Co.,Ltd., commercial name; Shinfluid 201).
- 20 • Polyolefin oil 5: The pour point is -35 °C. The kinematic viscosity at 40 °C is 420 mm²/s (produced by Exxon Mobil Corp., commercial name; Mobil SHF401).
- 20 Examples 1 through 8 and Comparison Examples 1 through 9
The grease and the polyolefin were mixed and kneaded at the ratios shown in tables 1 and 2 to obtain the lubricant grease, of each of the examples and the comparison examples, for low and high temperature application.
- 25 The penetration and dropping point of each lubricant grease

were measured. The cost per volume was also computed by setting the cost per volume of the lubricant grease of the comparison example 1 to one. Tables 1 and 2 show the results.

Each lubricant grease for low and high temperature application was sealed in a bearing 6203LLHA cleaned with petroleum benzine to obtain a rolling bearing of each example and comparison example. Each lubricant grease occupied 38% of the volume of the entire space in the bearing. The obtained rolling bearing was left in a low-temperature bath of -60 °C. When the temperature of the rolling bearing itself became -60 °C, it was taken out from the bath and placed in an atmosphere having room temperature. The rolling bearing was rotated at 2700 rpm (outer ring) under a radial load of 127 N to examine whether noises were generated before the rolling bearing became the room temperature. Results are shown in tables 1 and 2.

Each lubricant grease for low and high temperature application was sealed in a bearing 6204ZZ cleaned with petroleum benzine to obtain a rolling bearing of each example and comparison example. Each lubricant grease occupied 38 % of the volume of the entire space in the bearing. The obtained bearing was evaluated in a high-temperature durability test.

In the high-temperature durability test, the bearing was rotated under a radial load of 67 N and a thrust load of 67 N and at 10000 rpm and 180 °C to measure how long it took until a motor was stopped because of an overload. Results are shown

in tables 1 and 2.

Table 1

Table1

Component (parts by weight)	Example							
	1	2	3	4	5	6	7	8
Grease 1	40	40	40	40	40	40	40	40
Grease 2	-	-	-	-	-	-	-	-
Grease 3	60	60	60	60	60	60	60	60
Grease 4	-	-	-	-	-	-	-	-
Polyolefin oil 1	3	5	10	-	-	12	15	20
Polyolefin oil 2	-	-	-	3	-	-	-	-
Polyolefin oil 3	-	-	-	-	3	-	-	-
Properties								
Penetration	348	358	360	350	348	315	310	311
Dropping Point, °C	≥250	≥250	≥250	≥250	≥250	≥250	≥250	≥250
Noise at low temperature	N	N	N	N	N	N	N	N
High-temp. durability test(180 °C), h	≥4000	≥4000	≥4000	≥4000	≥4000	≥4000	≥4000	≥4000
Cost	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4

N:Not generated

5 Table 2

Table2

Component (parts by weight)	Example								
	1	2	3	4	5	6	7	8	9
Grease 1	100	-	-	40	40	40	40	40	40
Grease 2	-	100	-	-	-	-	-	-	-
Grease 3	-	-	100	60	60	60	60	60	-
Grease 4	-	-	-	-	-	-	-	-	60
Polyolefin oil 1	-	-	-	-	2	35	-	-	10
Polyolefin oil 4	-	-	-	-	-	-	5	-	-
Polyolefin oil 5	-	-	-	-	-	-	-	5	-
Properties									
Penetration	282	285	283	280	350	370	352	365	240
Dropping Point, °C	≥250	≥250	≥250	≥250	≥250	≥250	≥250	≥250	246
Noise at low temperature	Gen.	N	Gen.	Gen.	Gen.	N	N	Gen.	N
High-temp. durability test(180 °C), h	≥4000	3500	1400	≥4000	≥4000	1600	2000	≥4000	580
Cost	1.0	1.0	0.1	0.4	0.4	0.4	0.4	0.4	0.3

Gen.:Generated

N:Not generated

The lubricant grease, according to the present invention, for low and high temperature application contains the polyolefin

oil added to the mixed grease of the fluorine-containing lubricant grease and the urea-containing lubricant grease. Therefore by applying the lubricant grease for electric auxiliaries of a car and the like used at low and high temperatures, the lubricant 5 grease is durable owing to high resistance to high temperatures and capable of restraining noises from being generated at low temperatures.

Consequently the lubricant grease can be used suitably for rolling bearings for a fan clutch which is heated to very high 10 temperatures in the vicinity of 180 °C and an alternator which is used at high temperatures.